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IMPROVED FIBER RETENTION BY THE
USE OF FILLERS IN GRAPHITE FIBER/
RESIN MATRIX COMPOSITES

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GRAPHITE FIBER/RESIN MATRIX COMPOSITES

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ABSTRACT

A potential problem in the use of graphite fiber reinforced resin matrix composites is the dispersal of graphite fiber during accidental fires. Airborne electrically conductive fibers originating from burning composites could enter and cause shorting in electrical equipment located in surrounding areas. A variety of matrix fillers have been tested for their ability to prevent loss of fiber from graphite fiber/PMR polyimide and graphite fiber/epoxy composites in a fire. The fillers tested included powders of boron, boron carbide (B_4C), lime glass, lead glass, and aluminum. Of these fillers, boron was the most effective and prevented any loss of graphite fiber during burning. Mechanical properties of composites containing boron filler were measured and compared to those of composites containing no filler.

INTRODUCTION

Graphite fiber reinforced resin matrix composites are expected to gain widespread use in aerospace and automotive structural applications because of their lightweight and excellent strength properties (e.g., Refs. 1 and 2). However, there is concern that, in the event of accidental fires and possible associated explosions, electrically conductive graphite fibers may be dispersed and cause potential electrical hazards in neighboring electrical equipment (Ref. 3). A wide variety of approaches for composite modification to prevent this electrical shorting problem are being investigated, including resin modification, fiber modification, hybridization, and the use of particulate fillers. The purpose of this paper is to describe an investigation of the use of particulate fillers dispersed in the matrix to retard or prevent loss of graphite fiber from PMR polyimide matrix and epoxy matrix composites on burning. The general concept guiding selection of filler materials for testing was to select materials which would provide a melt at temperatures above the intended use temperature of the composite (preferably within a few hundred degrees above the use temperature). It was expected that the melt then would coat the graphite fibers and prevent them from becoming airborne. The candidate fillers selected and discussed in this report include powders of boron, boron carbide (B_4C), low softening temperature glasses, and aluminum. Although boron and boron carbide have high melting points (3812° and 4262° F, respectively), it was expected that they would be oxidized to boron trioxide (B_2O_3) which has the relatively low melting point of about 860° F. Boron trioxide was not selected as a filler because it is hygroscopic and probably would have adverse effects on composite properties.

Reference specimens of graphite/PMR polyimide composites containing no filler were fabricated. Other samples were fabricated containing each of the candidate fillers at a level of 10 percent of the graphite fiber weight present in the composite. Reference composite specimens of graphite/epoxy were prepared with no filler and additional specimens were fabricated with boron filler. Specimens were fire tested with an OSU Heat Release Rate Calorimeter and examined for loose surface fibers. Impact tests were conducted on selected composites and the amount of fiber release was also visually observed. Tests were conducted to measure the thermal oxidative stability, moisture resistance, and mechanical properties of as-fabricated laminates to discover any side effects of the use of boron filler.

EXPERIMENTAL

Materials

The filler materials selected for testing in composites were obtained from commercial sources. These filler materials and some of their properties are listed in Table I.

Commercially obtained Hercules HTS graphite yarn was used for preparation of the composite specimens. The matrix resins were: an addition-type polyimide (PMR-15) prepared from the monomers: (1) monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE); (2) 4,4' methylenedianiline (MDA); and (3) the dimethyl ester of 3,3', 4,4'-benzophenonetetracarboxylic acid (BTDE) (see Ref. 2); and a 350° F curing, commercially formulated, epoxy resin containing N,N,N',N' tetraglycidyl methylenedianiline and an aromatic amine curing agent.

Prepreg and Laminate Fabrication

The graphite fiber/PMR-15 prepreg was prepared by winding a three inch wide band of graphite yarn at a pitch of eight turns per inch on a 30 inch diameter drum (about 1.6 oz of fiber). The graphite was impregnated with a 50 w/o methanol solution of PMR-15. The filler materials were applied as a suspension in the monomer solutions. The filler was added in the amount of 10 percent of the fiber weight. The prepreg material was air dried at about 140° F until slightly tacky to the touch. The amounts of fiber and monomer in the prepreg were such as to yield cured composites containing 55 v/o fiber.

Graphite fiber/epoxy prepreg containing boron filler was prepared by winding a three inch wide band of graphite yarn at a pitch of seven turns per inch on a 30 inch diameter drum (1.4 oz of fiber). The fibers were then impregnated with a suspension of -325 mesh boron powder in a methylethyl ketone solution of the epoxy. The boron was added to yield composites containing boron nominally at 5, 10, 15, and 20 percent of the graphite fiber weight. Prepreg was also made containing no boron powder.

Nine ply unidirectional laminates, nominally 0.1 in. x 3 in. x 10 in. were fabricated by cutting and laying up prepreg plies. These layups were then staged, cured, and post-cured. In the case of graphite/PMR-15, the layups were staged at 400° F for 1 hour followed by a cure in a heated press at 600° F for 1 hour at 500 psi and a 16 hour post-cure at 600° F in air. In the case

of the graphite/epoxy layups, staging was carried out at 250° F until gelation occurred (about 30 min) and then curing was done at 350° F for 2 hours at 200 psi in a matched metal die mold followed by a post-cure for 4 hours at 400° F.

Laminate Testing

Room temperature flexural and interlaminar shear strength measurements were made on all as-fabricated filled and unfilled laminate specimens. Tests were also run on those laminates which were exposed to various environmental conditions. The span-to-depth ratio for the three point bend flexural specimens was 30:1 and for the shear specimens was 5:1. The environmental exposure of the graphite/epoxy specimens (with and without boron filler) consisted of 1032 hours in air at 400° F followed by an exposure of 1000 hours in 95 percent RH at 140° F.

Burning tests were carried out at Ohio State University. The test apparatus is described in Ref. 4 and shown in Fig. 1. The samples were heated on one face by a radiation source of 5.3 Btu/ft²-sec for 5 minutes in flowing air. The laminate specimens measured 0.1 in. x 3 in. x 6 in. Qualitative impact tests were done on the graphite/epoxy laminates after burning by striking the burned laminates with a hammer. The laminates were contained within a plastic bag when impacted.

RESULTS AND DISCUSSION

PMR/Filler Screening Studies

In this study, the evaluation of selected fillers for graphite/PMR-15 composites was based primarily on the amount of loose surface fibers that were produced during 5 minutes of exposure to a 5.3 Btu/ft²-sec radiative heat flux in the OSU Heat Release Rate Calorimeter.

Figures 2(a) to (f) summarize the results of the burning tests performed on PMR-15 laminates. The effectiveness of the filler material in providing fiber containment was determined by visual examination of the laminate surfaces exposed to the radiant heater. Also, the stiffness of the burned samples in the direction of the fiber was qualitatively evaluated. All of the filled composites retained some rigidity in the 0° fiber direction after being burned. The boron filled burned composite exhibited a shiny surface with no bare fibers discernible (Fig. 2(a)). In contrast, the burned reference sample of HTS/PMR-15 had a very soft fluffy surface of bare graphite fibers (Fig. 2(f)). All the other filled samples had surfaces varying in amount of exposed fibers between the conditions exhibited by the reference sample and the boron filled sample (Figs. 2(b) to (e)). Based on these results, filler materials were ranked in order of fiber retention effectiveness as follows:

1. Boron
2. B₄C
3. Lead glass
4. Lime glass
5. Aluminum

Boron Filler/Epoxy Laminate Burn Tests

Because of the promising results obtained with boron fillers in the PMR-15 matrix, boron was selected for study in a low char epoxy matrix. A series of graphite fiber reinforced panels were fabricated using Hercules 3501-6 epoxy matrix containing 0, 5, 10, 15, and 20 percent boron based on the total weight of fiber in the panel.

The results of burn tests on the epoxy laminates, two of which are shown in Fig. 3, were identical to the results from the burning of the boron filled graphite/PMR-15 specimens. Furthermore, no difference in appearance could be visually determined as to the quality of the surfaces for the 5, 10, 15, and 20 percent boron filled specimens. After impacting the samples, examination of the debris (Fig. 4) indicated that the burned residue of the resin and the boron was still firmly bonded to the graphite fibers so that no bare fibers were released.

The results of the burn and impact tests from the PMR-15 and epoxy laminates clearly demonstrated the excellent potential of boron powder as a means of improving the fiber retention properties of resin matrix composites. Thus, the remainder of the work was directed toward determining the effects of the boron powder filler on physical and mechanical properties of the composites.

Laminate Physical and Mechanical Properties

Table II presents the results of the room temperature flexural and interlaminar shear strength tests made on samples of the PMR-15 matrix composites containing four candidate filler materials. Each value is the average of three determinations. It was expected that all the particulate fillers would behave as voids and affect the strength values in approximately the same way. The glass powder and the aluminum powder had no apparent effect on the flexural strength as compared to the reference unfilled samples. The lime glass, however, did decrease the interlaminar shear strength significantly. Both B and B₄C reduced the flex strength by about 50 percent. All of the graphite/PMR-15 samples were examined metallographically and it was found that the boron and B₄C filled samples contained large concentrations of the powder at the surfaces of the specimens. This was confirmed by digesting samples of the composites sliced from the surfaces of the composite test specimens. The details of the digestion procedure are given in Ref. 5. This concentration of boron and B₄C at the laminate surface was thought to be responsible for the low flexural strengths. More importantly, however it suggested that this was a processing problem that could be eliminated by optimizing the fabrication process.

Table III shows the results of room temperature mechanical tests on the epoxy laminates in the as-fabricated condition, after aging at 400° F for about 1000 hours and also after exposure to 95 percent RH and 140° F for about 1000 hours. Also shown are weight changes from temperature and humidity exposure. The flexural strength, normalized to 60 volume percent of fiber (due to large differences in fiber content between the reference and boron filled laminates) and the ILSS were equivalent to the properties of the unfilled composites. For the epoxy laminates which were processed using a more closely controlled fabrication procedure than was used for the PMR-15 laminates, the boron filled material had no significant effect on the mechanical properties of the resin/fiber system.

The presence of the boron powder in the laminates caused no apparent increase in sensitivity of mechanical properties to air aging at 400° F or to 95 percent relative humidity at 140° F for times up to about 1000 hours.

Based on these results, use of boron powder additions to polymer matrices in graphite fiber reinforced composites appears to be an excellent method for reducing and/or eliminating fiber release from burning composites. Furthermore, this is a method which can be incorporated with minimal delay and minimal perturbation of composite materials.

CONCLUDING REMARKS

1. Addition of boron powder to the matrix of graphite/PMR-15 or of graphite/epoxy composites is an effective method for retaining graphite fiber in the composite upon burning.

2. The flexural and interlaminar shear strengths of as-fabricated and of thermally and humidity exposed specimens containing boron filler are comparable to those of unfilled specimens.

3. The promising results of this investigation warrant further study to optimize the formulation and processing procedures and also to more fully characterize the boron filled composite system.

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3. "Carbon Fiber Hazard Concerns NASA," Aviat. Week Space Technol., vol. 110, no. 10, March 5, 1979, pp. 47-50.
4. Ignition, Heat Release, and Noncombustibility of Materials, ASTM Special Technical Publication 502, American Society for Testing and Materials, 1972, pp. 119-134.
5. R. J. Jones, R. W. Vaughan, and E. A. Burns, "Thermally Stable Laminating Resins," TRW-16402-6012-RO-00, TRW Systems Group, Redondo Beach, Calif., NASA-CR-72984, February 1972, pp. 179-180.

TABLE I. - PROPERTIES OF FILLER MATERIALS

Filler	Nominal Particle Size (μm)	Purity (% by weight)	Specific gravity	Melt or softening Temp., $^{\circ}\text{F}$
Boron	44 (-325 M)	95 (as B)	2.34	3812
Boron carbide (B_4C)	44 (-325 M)	77.54 (as B)	2.52	4262
Aluminum	44 (-325 M)	99 (as Al)	2.70	1228
Solder glass (vitreous, contains lead oxide)	44 (-325 M)	-----	5.38	824
Soda-lime glass	44 (-325 M)	-----	2.5	1292

TABLE II. - ROOM TEMPERATURE MECHANICAL PROPERTIES OF AS FABRICATED

FILLED AND UNFILLED GRAPHITE/PMR-15 LAMINATES

Property	Graphite PMR-15	Graphite PMR-15 (boron filler)	Graphite PMR-15 (B_4C filler)	Graphite PMR-15 (lime glass filler)	Graphite PMR-15 (Al filler)
Interlaminar shear strength (psi)	14,765	12,000	13,090	7,400	13,800
Flex. strength (psi)	266,800	134,600	156,600	223,500	250,800
Flex. mod. (psi)	17.4×10^6	17.0×10^6	16.30×10^6	16.7×10^6	15.7×10^6

TABLE III. - ROOM TEMPERATURE PROPERTIES FOR UNFILLED AND
BORON FILLED GRAPHITE/EPOXY LAMINATES

Property	Graphite/epoxy			Graphite/epoxy and boron		
	As-Fab	1032 hr. at 400° F	1000 hr. at 140° F and 95% RN	As-Fab	1032 hr. at 400° F	1000 hr. at 140° F and 95% RN
Interlaminar shear strength (psi) ^a	12,399	12,272	11,861	11,698	10,225	11,457
Flex. strength ^a (psi)	221,978	223,957	215,932	234,760	233,548	231,611
% weight change ^b	-----	-0.90	+1.50	-----	-1.00	+2.00

^aAverage of three determinations. Normalized to 60 volume percent fiber.

^bAverage of four determinations.

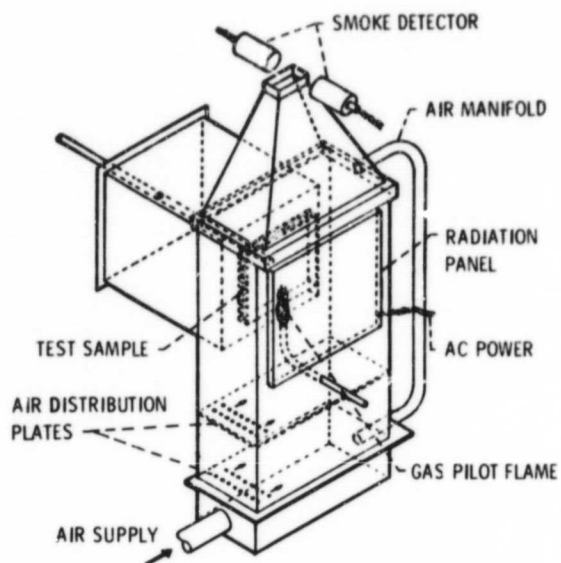
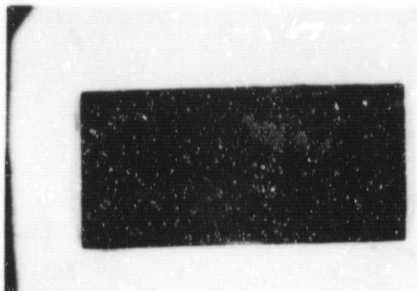
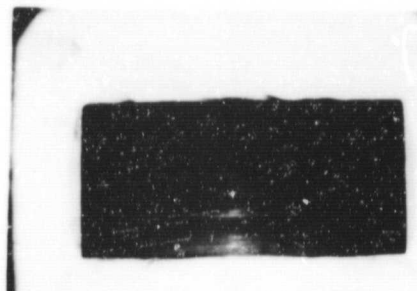


Figure 1. - OSU heat release rate calorimeter.

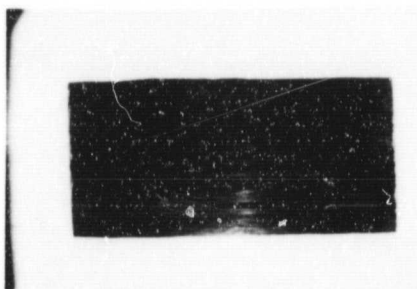
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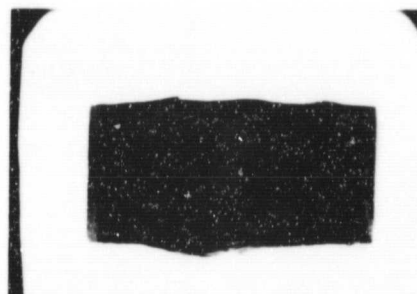
(a) BORON FILLER



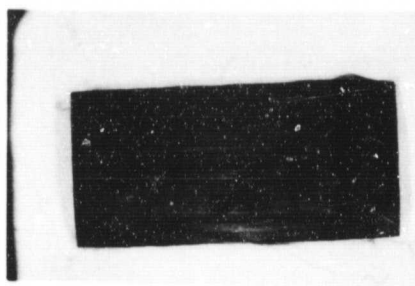
(d) LEAD GLASS FILLER



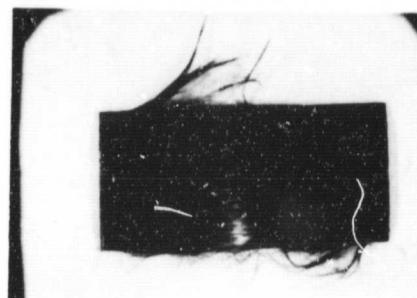
(b) B₄C FILLER



(e) ALUMINUM FILLER



(c) LIME GLASS FILLER

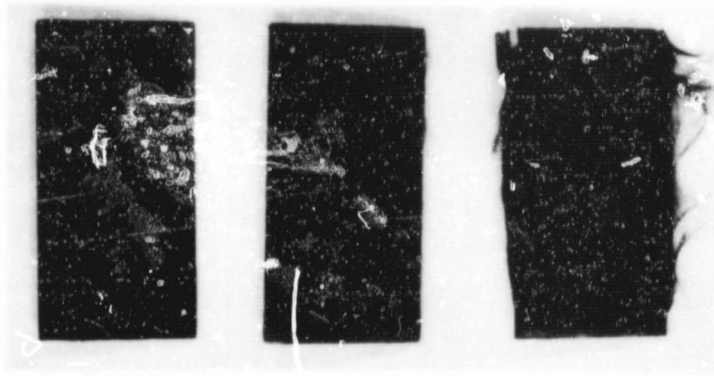


(f) UNFILLED

Figure 2. - Surfaces of HTS/PMR-15 laminates after exposure to 5.3 Btu/ft²-sec radiant heat for 5 minutes.

Figure 2. - Concluded.

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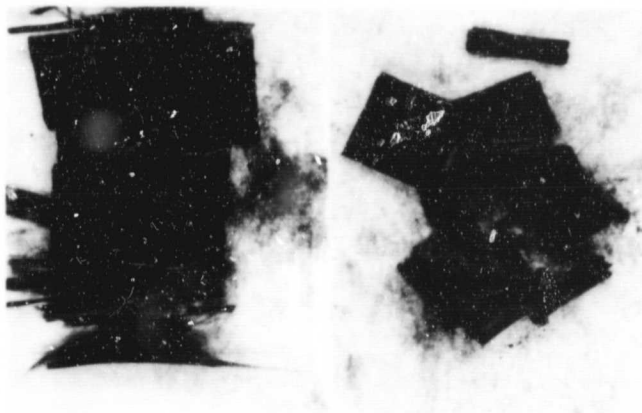


AS FABRICATED
(NOT BURNED)

WITH 10% BORON
(BURNED)

NO BORON
(BURNED)

Figure 3. - Improved fiber retention of burned graphite/epoxy laminates with boron filler (exposed to 5.3 Btu/ft²-sec radiation for 5 minutes).



NO BORON

WITH BORON

Figure 4. - Improved fiber retention of burned and impacted graphite/epoxy laminates with boron filler.